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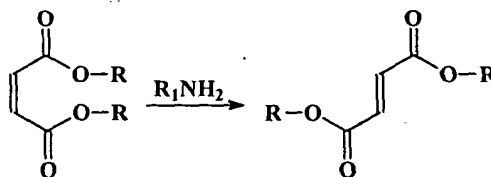
IN-SITU PREPARATION OF POLYASPARTIC ESTER MIXTURE FIELD OF THE INVENTION

The invention relates to a method for making polyaspartic esters.

BACKGROUND OF THE INVENTION

Two-component coating compositions having a polyisocyanate component and an isocyanate-reactive component (a polyhydroxyl component) are known. These compositions are suitable for the preparation of high quality coatings that may be rendered rigid, elastic, resistant to abrasion and to solvents and, above, all, resistant to weathering. Polyaspartic esters have been used as isocyanate-reactive components in such two-component compositions. A polyaspartic ester can be used individually, with a polyisocyanate, or possibly in combination with polyols or polyamines. Alternatively, polyaspartic esters can be used with blocked polyamines such as ketimines, aldimines or oxizolidines.

Methods for making polyaspartic esters are known. It is known, for instance, that during the Michael Addition Reaction of an ester of fumaric or maleic acid and the primary amine, for instance, the ester of maleic or fumaric acid isomerizes to dialkyl fumarate in the presence of amines, according to the following chemical reaction:



The dialkyl fumarate is then converted to a polyaspartic ester. Mixtures of polyaspartic esters based on cyclic and acyclic amines have proven to be valuable isocyanate-reactive components of polyurea compositions that have found utility in the formulation of high solids coatings where solvent content is very low or zero. These formulations are used in architectural and automotive refinish applications. Known methods for preparing polyaspartic ester mixtures typically involve preparing polyaspartic esters

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based on acyclic and cyclic amines separately and then combining each polyaspartic ester mixture. Polyaspartic esters based on acyclic amines, which contain amines attached to primary carbons, generally react with an isocyanate faster than polyaspartic esters based on cyclic amines that

5 have an amine group attached to a secondary ring carbon. In addition, polyaspartic esters based on acyclic amines have a lower viscosity than polyaspartic esters based on cyclic amines. It is often desirable to blend these types of amines to achieve formulations with different viscosities and with intermediate reaction speeds.

10 U.S. Pat. No. 5,236,741 and U.S. Pat. No. 5,623,045 each disclose a single step process for the production of polyaspartic esters. Each process reacts an ester of maleic or fumaric acid with a primary polyamine such that preferably one olefinic double bond is present for each primary amino group. The patents teach that excess starting materials is removed

15 by distillation after the reaction. Neither patent discusses how much time it takes for the reaction of the ester of maleic or fumaric acid to complete, i.e., to obtain a yield of about 100% of the polyaspartic ester. Neither patent addresses the issue of developing a process that makes a 100% yield of a mixture of (1) a polyaspartic ester based on a cyclic amine and

20 (2) a polyaspartic ester based on an acyclic amine in a matter of days.

Unfortunately, such methods have prevented manufacturers of polyaspartic esters from delivering shipments to customers as quickly as would be desired. I have discovered that by following the teachings of the above-described known methods and using a 1:1 stoichiometric ratio, it

25 takes several months to obtain full, or near-full, conversion of the reaction of a cyclic amine and an ester of maleic or fumaric acid. For instance, the use of bis (4-aminocyclohexyl)methane requires the polyaspartic ester to be stored in excess of six weeks to achieve 95% reaction and from six to twelve months to achieve complete reaction; and the use of bis (3-methyl-

30 4-aminocyclohexyl)methane [commercially known as Laromin C-260] requires the polyaspartic ester to be stored in excess of eight weeks to achieve 95% reaction and from twelve to eighteen months to achieve 100% reaction. Removing excess ester of maleic or fumaric acid, as suggested by U.S. Pat. Nos. 5,236,741 and 5,623,045, is a time-

35 consuming expensive procedure.

The problem of long waiting times has not been able to be resolved by making large amounts of the mixtures in advance because it is extremely difficult to predict customers' needs for the mixtures. Further, expensive storage, and inventory costs have discouraged the making and the storing of large amounts of the mixtures. As such, it is not uncommon for a customer to have to wait several months to receive an order of mixtures of polyaspartic esters.

It would be advantageous to develop an improved method for making mixtures of polyaspartic esters based on cyclic amines and polyaspartic esters based on acyclic amines that overcomes the above-named disadvantages.

SUMMARY OF THE INVENTION

The invention relates to a method for making a polyaspartic ester mixture *in-situ* comprising the sequential steps of (a) reacting a cyclic amine with an excess amount of an ester of fumaric or maleic acid to form a mixture containing first polyaspartic ester component and excess unreacted ester of fumaric or maleic acid, and (b) adding an acyclic amine to the mixture resulting from step (a) and reacting the acyclic amine with the excess ester of fumaric or maleic acid to form a second polyaspartic ester component. The invention is also directed to the *in-situ* mixture of polyaspartic ester esters formed during the method, prior to termination of the process, that contains the first polyaspartic ester component and the second polyaspartic ester component. The method makes it possible for customers to receive mixtures of the polyaspartic esters in a fraction of the time it has ordinarily taken. These and other features, aspects, and advantages of the present invention will become better understood with reference to the following description and appended claims.

DETAILED DESCRIPTION OF THE INVENTION

As used in this application, the term "cyclic amine" refers to an amine that has at least one primary amine group attached to a cyclic group, e.g., an amine attached to a secondary ring carbon. The term "acyclic amine" refers to an amine that does not have a primary amine group attached to a cyclic.

The invention is based on the discovery that mixtures of polyaspartic esters based on cyclic amines and polyaspartic esters based on

acyclic amines can be prepared *in-situ*, (under certain conditions) in a fraction of the time it ordinarily takes to make them. It is critical that the cyclic amine first react with an excess ester of maleic or fumaric acid. As discussed below, if the sequence of the steps varies, e.g., if the steps are reversed or if the cyclic and acyclic amines are added simultaneously, the reaction proceeds substantially slower and is outside the scope of the present invention.

The first and second ester components are selected from esters of maleic acid and fumaric acid. Esters of maleic acid and fumaric acid include suitable dialkyl maleates or dialkyl fumarates. Suitable dialkyl maleates include, diethyl maleate, dipropyl maleate, dibutyl maleate, methyl propyl maleate, ethyl propyl maleate, and the like. Suitable dialkyl fumigates include, diethyl fumurate, dipropyl fumurate, dibutyl fumurate, methyl propyl fumurate, ethyl propyl fumurate, and the like. Generally, dimethyl maleate or dimethyl fumurate is not used in an appreciable amount because it has been discovered that these esters cause the precipitation of long needle-like crystals that no longer participate in the Michael Addition Reaction and that cause the reaction to stop altogether. It is believed that cinnamate esters do not react under the same reaction conditions as esters of maleic acid or fumaric acid.

The amine component is generally selected from difunctional or trifunctional cyclic and acyclic amines that can accomplish the objects of the invention. Suitable amines can be selected from the following. Suitable acyclic difunctional amines include but are not limited to ethylene diamine, 1,2-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 2,5-dimethylhexane, 2,2,4- and/or 2,4,4-trimethyl-1,6-diaminohexane, 1,11-diaminoundecane, 1,12-diaminododecane, 1-amino-3,3,5-trimethyl-5-aminomethylcyclohexane, 2,4- and/or 2,6-hexahydrotolylenediamine, 2,4'- and/or 4,4'-diaminodicyclohexylmethane, and 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane. Suitable cyclic amines include aromatic polyamines such as 2,4- and/or 2,6-diaminotoluene, and 2,4'- and/or 4,4'-diaminodiphenyl-methane are also suitable but less preferred. Other suitable cyclic amines include Bis- (3-methyl-4aminocyclohexyl) methane, 2,4-diamino-1-methyl, cyclohexane, and 2,6-diamino-1-methyl cyclohexane.

Suitable trifunctional amines include 4-aminomethyl-1,8-diaminooctane (also known as triaminononane supplied by Monsanto Company), tris-(2-aminoethyl)amine. It is believed that tetrafunctional amines, e.g., N,N,N',N'-tetrakis-(2-aminoethyl)-1,2-ethanediamine are also
5 suitable.

The polyisocyanate component used to react with the polyaspartic ester mixtures includes any polyisocyanate, which when used in accordance with the invention, meets the object of the invention. Suitable polyisocyanates for use as polyisocyanate component in accordance with
10 the present invention include the known polyisocyanates of polyurethane chemistry. Examples of suitable low molecular weight polyisocyanates having a molecular weight of 168 to 300 include 1,4-diisocyanatobutane, 1,6-hexamethylene diisocyanate, 2,2,4- and/or 2,4,4-trimethyl-1,6-hexamethylene diisocyanate, dodecamethylene diisocyanate, 1,4-
15 diisocyanatocyclohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI), 2,4'- and/or 4,4'-diisocyanato-dicyclohexyl methane, 2,4- and/or 4,4'-diisocyanatodiphenyl methane and mixtures of these isomers with their higher homologues that are obtained in a known manner by the phosgenation of aniline/formaldehyde condenses, 2,4-
20 and/or 2,6-diisocyanatotoluene and any mixtures of these compounds. Preferred cyclic isocyanates include diphenylmethane 4,4'-diisocyanate (MDI), diphenylmethane 2,4'-diisocyanate, 2,4- and/or 2,6-diisocyanatotoluene. Preferred aliphatic isocyanates include hexamethylene diisocyanate, isophorone diisocyanate, 2,4'- and/or 4,4'-diisocyanato-dicyclohexyl
25 methane.

Additional suitable polyisocyanate components include derivatives of the above-mentioned monomeric polyisocyanates, as is conventional in coatings technology. These derivatives include polyisocyanates containing biuret groups as described, for example, in U.S. Pat. Nos. 3,124,605
30 and 3,201,372 and DE-OS 1,101,394, incorporated herein by reference in their entirety; polyisocyanates containing isocyanurate groups as described in U.S. Pat. No. 3,001,973, DE-PS 1,022,789, 1,222,067 and 1,027,394 and DE-OS 1,929,034 and 2,004,048, incorporated herein by reference in their entirety; polyisocyanates containing urethane groups as
35 described, for instance, in DE-OS 953,012, BE-PS 752,261 and U.S. Pat. Nos. 3,394,164 and 3,644,457; polyisocyanates containing carbodiimide

groups as described in DE-PS 1,092,007, U.S. Pat. No. 3,152,162 and DE-OS 2,504,400, 2,537,685 and 2,552,350, incorporated herein by reference in their entirety; and polyisocyanates containing allophanate groups as described, for example, in GB-PS 994,890, BE-PS 761,626 and 5 NL-OS 7,102,524. Suitable polyisocyanates also include polyisocyanates that contain uretdione groups. In one embodiment, asymmetric trimers such as those in U.S. Pat. No. 5,717,091, incorporated herein by reference in its entirety. Isocyanate group-containing prepolymers and semi-prepolymers based on polyisocyanates can also be used as the 10 polyisocyanate component. These prepolymers and semi-prepolymers generally have an isocyanate content ranging from about 0.5 to 30% by weight, preferably about 1 to 20% by weight, and are prepared in a known manner by the reaction of starting materials, e.g., isocyanate-reactive compounds such as polyols, at an NCO/OH equivalent ratio of about 15 1.05:1 to 10:1, preferably about 1.1:1 to 3:1.

The first step of the process involves reacting a cyclic amine with an excess amount of an ester of fumaric or maleic acid to form a mixture containing first polyaspartic ester component and excess unreacted ester of fumaric or maleic acid. The equivalent ratio of the ester of maleic or 20 fumaric acid to the cyclic polyamine is greater than 1:1, preferably 1.2:1 to 5:1 and more preferably 1.4:1 to 3:1. Generally, the more excess ester of maleic or fumaric acid used, the faster the initial reaction proceeds. To obtain a yield that is about 100% at a ratio of ester of maleic or fumaric acid to cyclic amine of 2:1, for instance, the reaction lasts less than 24 25 hours. When the number ratio of ester of maleic or fumaric acid to cyclic amine of 5:1, for instance, the reaction lasts less than 8 hours. It is generally preferred to have the initial reaction to be complete in about eight hours. Actual ratios for a specific application can be determined by routine experimentation.

30 The second step of the process involves adding an acyclic amine to the mixture and reacting the acyclic amine with the excess ester of fumaric or maleic acid to form a second polyaspartic ester component. The acyclic amine is preferably used in an amount that corresponds to the excess, unreacted ester of fumaric or maleic acid. Accordingly, the 35 equivalent ratio of acyclic amine to cyclic amine is preferably 0.2:1 to 4:1,

preferably 0.4:1 to 2:1. The reaction of the excess ester of maleic or fumaric acid and the acyclic amine generally takes less than two weeks.

5 The reaction conditions at which the method is carried out under are discussed below. Generally, the reaction takes place at a temperature of 0 to 100°C. The reaction may take place in the absence or in the presence of suitable solvents such as methanol, ethanol, propanol, ethyl- or butyl acetate and mixtures of these solvents. The pressure of the reaction is generally atmospheric. As such, since the reaction of the cyclic polyamine and the ester of maleic or fumaric acid lasts hours instead of 10 months, conversions of about 100% of mixtures of the polyaspartic ester based on the cyclic amine and the polyaspartic ester based on the acyclic amine can be obtained in days instead of months. Generally, a conversion of about 100% is obtained in less than 10 to 14 days.

15 The polyaspartic ester mixtures can be used in applications such as coatings. The low viscosity allows the formulation of paint at high or very high solids, or even paint with no solvent. Coatings applications can use polyurea coatings based on polyaspartic esters and polyisocyanates include general factory applied coating and field applied architectural or automotive refinish coatings.

20 The invention will now be described in the following illustrative examples. All percentages given are by weight unless otherwise indicated.

EXAMPLE 1

25 A round bottom flask was fitted with stirrer, thermocouple, addition funnel and nitrogen inlet. 75.6 g (0.720 eq) bis *p*-aminocyclohexyl methane (PACM) was admitted to the flask. 348.7 g (2.024 eq) diethyl maleate was admitted to the flask via the addition funnel over a one hour period. The temperature of the reaction mixture rose to 60°C as a result of a reaction exotherm. The temperature was maintained at 60°C for an 30 additional five hours. The unsaturation number was 35.7 mg maleic acid per gram of resin, which indicated 100% of the PACM had been converted to aspartate. 75.6 g (1.304 eq) 1,6-hexanediamine was added to the reaction over a forty-five minute period. The reaction was heated at 60°C for four hours when the unsaturation number was 1.05, which indicated

To determine the extent of the reaction, the unsaturation number was determined by a thiol-iodine titrametric method. This method titrates all double bonds so that the sum of both maleic and fumaric esters is included in the resultant unsaturation number. The units of unsaturation number is given in terms of milligrams maleic acid per gram of resin. Twenty-four hours later the unsaturation number was 0.66, which indicated the reaction was 98% complete.

Calculations were made in accordance to the following formula:

$$\text{maleic acid number (mg per g resin)} = \frac{(\text{blank volume} - \text{sample volume}) 1.161}{\text{sample weight}}$$

This example demonstrates the difference between Sequential of Example 1 and the reverse order of sequential mixing PACM and HDA). The procedure of Example 1 was repeated as follows. A round bottom flask was fitted with stirrer, thermocouple, addition funnel and nitrogen inlet. 50.0 g (0.862 eq) 1,6-hexanediamine (HDA) was admitted to the flask. 230.1 g (1.338 eq) diethyl maleate was admitted to the flask via the addition funnel over a one and one half hour period. The temperature of

the reaction mixture rose to 60°C as a result of a reaction exotherm. The temperature was maintained at 60°C for an additional four and one half hours. The unsaturation number was 20.0 mg maleic acid per gram of resin, which indicated 99.8 % of the HDA had been converted to

5 aspartate.

50.0 g (.862 eq) bis *p*-aminocyclohexyl methane (PACM) was added to the reaction over a thirty minute period. The reaction was heated at 45°C for four and one half hours when the unsaturation number was 11.44, which indicated the reaction with PACM was 42 % complete. At the
10 end of one week the unsaturation number was 5.05, which indicated the reaction with PACM was only 75 %complete. At the end of one month the unsaturation number was 1.95, which indicated the reaction was only 90% complete.

COMPARATIVE EXAMPLE B

15 This example demonstrates the difference between sequential process Example 1 and concurrent mixing of PACM and HDA. The procedure of Example 1 was repeated as follows. A round bottom flask was fitted with stirrer, thermocouple, addition funnel and nitrogen inlet. 50.0 g (0.476 eq) PACM and 50.0 g (0.862 eq) 1,6-hexanediamine was admitted to the flask
20 at 40°C and mixed for five minutes. 230.1 (1.338 eq) diethyl maleate was admitted to the flask via the addition funnel over a two hour period. The temperature of the reaction mixture rose to 60°C as a result of a reaction exotherm. The reaction was held at 60°C for an additional four hours. The unsaturation number was 15.82 mg maleic acid per gram of resin, which
25 indicated 84.0 % of the maleate had been converted to aspartate. If it is assumed that 90 % of the hexanediamine had been converted, this means that only 23 % of the PACM had been converted. After one month the unsaturation number was 1.83, which indicated 94 % of the maleate had been converted to aspartate. If it is assumed that 100 % of the
30 hexanediamine had been converted, this means that only 89 % of the PACM had been converted after one month.

EXAMPLE 2

The procedure of Example 1 was repeated as follows. A round bottom flask was fitted with stirrer, thermocouple, addition funnel and

nitrogen inlet. 50.0 g (0.476 eq) bis *p*-aminocyclohexyl methane (PACM) was admitted to the flask. 230.1 g (1.338 eq) diethyl maleate was admitted to the flask via the addition funnel over a one and one half hour period.

5 The temperature of the reaction mixture rose to 40°C as a result of a reaction exotherm. The temperature was maintained at 40°C for an additional four and one half hours. The unsaturation number was 36.0 mg maleic acid per gram of resin, which indicated 99.5 % of the PACM had been converted to aspartate.

10 50.0 g (.862 eq) 2-methyl-1,5-pentane diamine (available from DuPont as Dytek A) was added to the reaction over a forty-five minute period. The reaction was heated at 45°C for four and one half hours when the unsaturation number was 4.87, which indicated the reaction was 87 % complete. At the end of one week the unsaturation number was zero, which indicated the reaction was complete.

15 COMPARATIVE EXAMPLE C

The procedure of Example 2 was repeated as follows. A round bottom flask was fitted with stirrer, thermocouple, addition funnel and nitrogen inlet. 150.0 g (1.43 eq) PACM and 150.0 g 2-methyl-pentane-diamine (Dytek A, available from Dupont) were admitted to the flask and
20 mixed for five minutes. 689.7 g (4.01 eq) diethyl maleate was admitted to the flask via the addition funnel over a one hour period. The temperature of the reaction mixture rose to 60°C as a result of a reaction exotherm. The reaction was held at 60°C for an additional five and one half hours. The unsaturation number was 4.35 mg maleic acid per gram of resin,
25 which indicated 90.7% of the maleate had been converted to aspartate. If it is assumed that 95% of the 2-methylpentane-diamine had been converted, this means that only 83% of the PACM had been converted.

After 11 days, the unsaturation number was 1.52, which indicated 96.8% of the maleate had been converted to aspartate. If it is assumed
30 that 100% of the 2-methylpentane-diamine had been converted, this means that only 90.1% of the PACM had been converted after 11 days. After 18 days, the unsaturation number was 0.43, which indicated 99.1% of the maleate had been converted to aspartate. If it is assumed that 100% of the 2-methylpentane-diamine had been converted, this means
35 that 97.4% of the PACM had been converted after 18 days.

The conversion of PACM to aspartate occurred at about the same rate as if the Dytex were not present.

COMPARATIVE EXAMPLE D

5 This example demonstrates the difference between the sequential
process of Example 2 and the reverse order of sequential mixing PACM
and Dytex A. A round bottom flask was fitted with stirrer, thermocouple,
addition funnel and nitrogen inlet. 50.0 g (0.862 eq) 2-methyl-1,5-pentane
diamine (available from DuPont as Dytex A) was admitted to the flask.
230.1 g (1.338 eq) diethyl maleate was admitted to the flask via the
10 addition funnel over a one and one half hour period. The temperature of
the reaction mixture rose to 60°C as a result of a reaction exotherm. The
temperature was maintained at 60°C for an additional four and one half
hours. The unsaturation number was 19.6 mg maleic acid per gram of
resin, which indicated 100 % of the HDA had been converted to aspartate.
15 50.0 g (.862 eq) bis *p*-aminocyclohexyl methane (PACM) was added to
the reaction over a thirty minute period. The reaction was heated at 45°C
for four and one half hours when the unsaturation number was 12.26,
which indicated the reaction with PACM was 37 % complete. At the end of
one week the unsaturation number was 4.17, which indicated the reaction
20 with PACM was only 79 %complete. At the end of one month the
unsaturation number was 1.92, which indicated the reaction was only 90%
complete.

Although the invention has been described in detail in the foregoing
for the purpose of illustration, it is to be understood that such detail is
25 solely for that purpose and that variations can be made therein by those
skilled in the art without departing from the spirit and scope of the
invention except as it may be limited by the claims.